

Environmental impacts of petroleum production: Results from the OSPER “A” site, Osage County, Oklahoma, USA

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ABSTRACT: Exploration for and production of petroleum have caused major environmental damage to soils, surface and ground waters and the local ecosystems worldwide. About 20 scientists from various disciplines are investigating the transport, fate, and natural attenuation of inorganic salts, organic compounds and radionuclides present in produced water, and their impacts at the Osage-Skiatook Petroleum Environmental Research sites, located in Osage County, Oklahoma. Results from the depleted “A” site show that: 1- the salts have been removed from the soil and surficial rocks, but weathered oil persists on the surface, especially in the old oil and brine pits and close to old tanks; 2- a plume of high salinity water (2,000-25,000 mg/L TDS) is present at intermediate depths that extend from the old oil and brine pits to Skiatook Lake; 3- soluble petroleum byproducts, including organic acid anions, BTEX and other VOCs are present in the contaminated groundwater; 4- the chemical composition of released brines is modified by sorption, mineral precipitation/dissolution, transpiration, volatilization and bacterially mediated oxidation/reduction reactions, in addition to mixing with pristine groundwater; and 5- significant amounts of salts remain in the soils and rocks of the impacted area after >65 years of natural attenuation.

1 INTRODUCTION

Oil and natural gas currently are the main sources of primary energy in the USA, supplying about 63% of the energy consumption, and forecasts indicate that by 2025 their consumption will increase by 48 and 50%, respectively (EIA 2003). A total of ~3.5 million oil and gas wells have been drilled in 36 states since 1859, but currently only about 880,000 are in production (Kharaka et al. 1995, Otton et al. 2002). Petroleum production, drilling operations, and improperly sealed abandoned wells have caused major contamination of surface and ground waters and soils in energy producing states (Richter & Kreitler 1993, Kharaka et al. 1995).

Prior to the institution of Federal regulations in the 1970's, produced waters, which could be highly saline (TDS may exceed 350,000 mg/L), may contain toxic metals, organic and inorganic components, and ^{226}Ra , ^{228}Ra and other naturally occurring radioactive materials (NORM), were often discharged into streams, creeks and unlined evaporation ponds causing salt scars and surface and ground water pollution (Kharaka et al. 1995, Otton et al. 2002). Contamination today results mainly from the improper disposal of large volume (currently 20-30 billion bbl/year) of saline water produced with oil and gas, and from hydrocarbon and produced water releases

caused by equipment failures, vandalism, and accidents (Kharaka & Hanor 2003, Otton & Zielinski 2003). These releases and the improper disposal of produced water have become important national and worldwide issues (USEPA 1987, Carty et al. 1997).

For several years, ~20 scientists from the USGS and other governmental agencies and academia have been conducting a multidisciplinary investigation to study the transport, fate, and natural attenuation of inorganic salts, trace metals, organic compounds and radionuclides present in produced water and oil releases, and their impacts on soil, surface and ground waters and the local ecosystem at the Osage-Skiatook Petroleum Environmental Research (OSPER) “A” (depleted) and “B” (depleting) sites, located in Osage County, OK (Kharaka & Otton 2003). In this report, we discuss the scientific approaches used and summarize the main results obtained to date from the “A” site. Such detailed studies may serve to guide estimates of human and ecosystem risk at these and similar sites and to develop risk-based corrective actions, which are particularly needed in aging and depleted fields, where land use is changing from petroleum production to residential, recreational, agricultural or other uses (Carty et al. 1997).

2 OSPER “A” SITE

The “A” site, located within the larger Lester Lease, has an area of ~1.5 hectare that is impacted by produced water and hydrocarbon releases that occurred primarily 60-90 years ago. The site is underlain by (1) a surface layer of eolian sand (0-120 cm); (2) colluvium that ranges from large boulders of sandstone to thin, granule-pebble conglomerate; (3) weathered shale, siltstone, and sandstone; and (4) underlying unweathered shale, siltstone and sandstone. Much of the site appears to have been impacted by early salt-water releases that limited colonization of young oak trees in an originally open area with scattered older oak trees. The gently sloping upper part of the site is slightly eroded in places and has been mostly revegetated with grasses, forbs, sumac, and a few trees. The lower, steeper, more heavily salt-impacted portion has been eroded to depths of as much as 2 m. Seepage of saline water from a shallow sandstone aquifer continues and active salt scarring persists (Otton & Zielinski 2003).

Drilling on the Lester Lease started in 1912, and oil production, which was from the Bartlesville sand at depths of 450-524 m, ended about 10 years ago. Most of the >100,000 bbl of oil produced by 1981, was obtained prior to 1937. Oil and produced water collected in two redwood tanks at the top of the site were transported via ditch to two roadside pits at mid-site. Produced water and hydrocarbon (now highly degraded and weathered oil) releases from pipeline breaks and tank batteries, that are no longer present, are scattered around the site. However, one pit at this site contains relatively fresh asphaltic oil and high salinity brine (Godsy et al. 2003, Kharaka et al. 2003).

2.1 Field methodology

Intensive investigations aimed at mapping and characterizing the geology, hydrology, contaminant sources and impacted areas at the OSPER “A” site and the immediate surrounding areas have continued since February 2001 (Kharaka & Otton 2003). Groundwater impacts are being investigated by repeated sampling of 35 wells (1-36 m deep), completed with slotted PVC tubing. The well locations were chosen on the basis of: (1) the presence of salt scars, excessive soil and rock erosion, brine and asphalt pits, degraded oil, dead trees and shrubs and other visible surface features; (2) results of electrical conductance, Cl, Br and SO₄ measurements on aqueous leachates from samples of shallow soil (0-15 cm), selected soil profiles (0.5-1.7 m) and core samples from prior drilled wells; and (3) results of electromagnetic (EM) and DC resistivity surveys used to map the subsurface distribution of salt in groundwater, soil and bedrock (Smith et al. 2003).

The mineral composition and sorption properties of selected core samples from impacted and “pristine” areas were investigated by Rice et al. (2003). The concentrations of nitrates, organic matter, total petroleum hydrocarbons (TPH), conductivity, chlorides, and dehydrogenase activity (DHA) were determined in selected grab and core samples from impacted and “pristine” areas; these parameters are essential for the development of remediation guidelines (Kampbell et al. 2003). A series of oil, water, brine, and soil samples were characterized and analyzed for geochemical parameters that are indicative of microbial activity. Characterization of the resident microbial populations and the varying stages of weathering and biodegradation of oils were reported by Godsy et al. (2003). The rate of salt removal from the site by surface runoff is being determined by measuring the volume and chemical composition of water flowing over a weir installed close to the Skiatook reservoir in a location that captures most of the surface and ‘base’ flow from this site following precipitation.

3 RESULTS AND DISCUSSION

Results to date show that impacts of produced water and associated hydrocarbons on soil and ground and surface waters are widespread at the site. All wells show some degree of contamination from produced water and/or associated petroleum or its degradation products. Thus, it has been very difficult to obtain soil and water samples from “pristine” areas. A “background” well, drilled 0.6 km to the NW of the OSPER “A” site initially (March, 2001) had fresh-water (450 mg/L TDS), low DOC values and other characteristics of the pristine local groundwater. Repeated sampling did not change the inorganic composition of water from this well significantly, but DOC concentrations have increased over time. Our latest (June 2003) sample from this well showed no significant change in the inorganic solutes, but small oil globules and relatively high concentrations of DOC, BTEX and other VOCs were obtained.

Results of water samples from nearby oil wells indicate that the produced water source is a Na-Ca-Cl brine (~150,000 mg/L TDS), with relatively high concentrations of Mg, Sr, Fe, Mn and NH₄, but low concentrations of SO₄, H₂S and dissolved organics. The chemical composition of Skiatook Lake water and groundwater in the area not impacted by petroleum operations shows major contrast from that of produced water. The water is fresh (150-520 mg/L TDS), has much higher Mg and Ca concentrations relative to Na, and much higher HCO₃ and SO₄ relative to Cl, when compared to source produced water; it is oxic, with low concentrations of metals, including Fe and Mn, as well as low DOC and organic anions (Kharaka et al. 2003).

Results show that the area source oils are paraffinic-naphthenic light oil (~35 API), containing *n*-alkanes as the dominant components unimpacted by biodegradation. The oils at the inactive “A” site are similar although they vary in stages of biodegradation. Microbial populations are degrading the water-soluble crude oil compounds. The geochemical evidence and make-up of the microbial populations indicate that the systems are poised at the level of iron reduction (Godsy et al. 2003). An important result from this investigation is the fact that high salinity groundwater plumes mapped on the basis of chemical analysis of water are in general agreement with those obtained from aqueous leachate data from soil and core samples as well as from the geophysical surveys (Kharaka & Otton 2003).

Results at the “A” site show that the salts have essentially been removed from the soil and surficial sediments, but degraded and weathered oil persists on the surface of old oil and brine pits, close to sites of old tanks, on old channels that carried oil from tanks to the oil pits and other impacted areas. Results also show a plume of high salinity water (2,000-25,000 mg/L TDS) is present at intermediate

depths and extends from below the old oil and brine pits (Fig. 1) to Skiatook Lake. No liquid petroleum was found in the contaminated groundwater, but soluble petroleum byproducts, including organic acid anions, BTEX and other VOCs are present.

We expect that detailed geological, geophysical, hydrologic, geochemical and ecological studies at these two sites will continue for 3-5 more years, with the emphasis shifting from site characterization to investigating the relevant hydrogeochemical processes and determining the rates of transport and degradation of solutes, using solute transport modeling. Additional deep drilling, however, is needed at the OSPER “A” site to map the depth and the horizontal boundaries of the 3-D plume of high salinity water (2,000-25,000 mg/L TDS) with chemical and isotopic characteristics similar to those of the source produced water (Fig. 1). The depth of this plume is not currently well defined; the one well that penetrates into a deeper aquifer (A-02) has lower salinity (2,000 mg/L TDS), but high Fe, Mn and dissolved organics. The horizontal plume boundaries are also not well delineated, because all wells deeper than 2 m at the site encounter the plume.

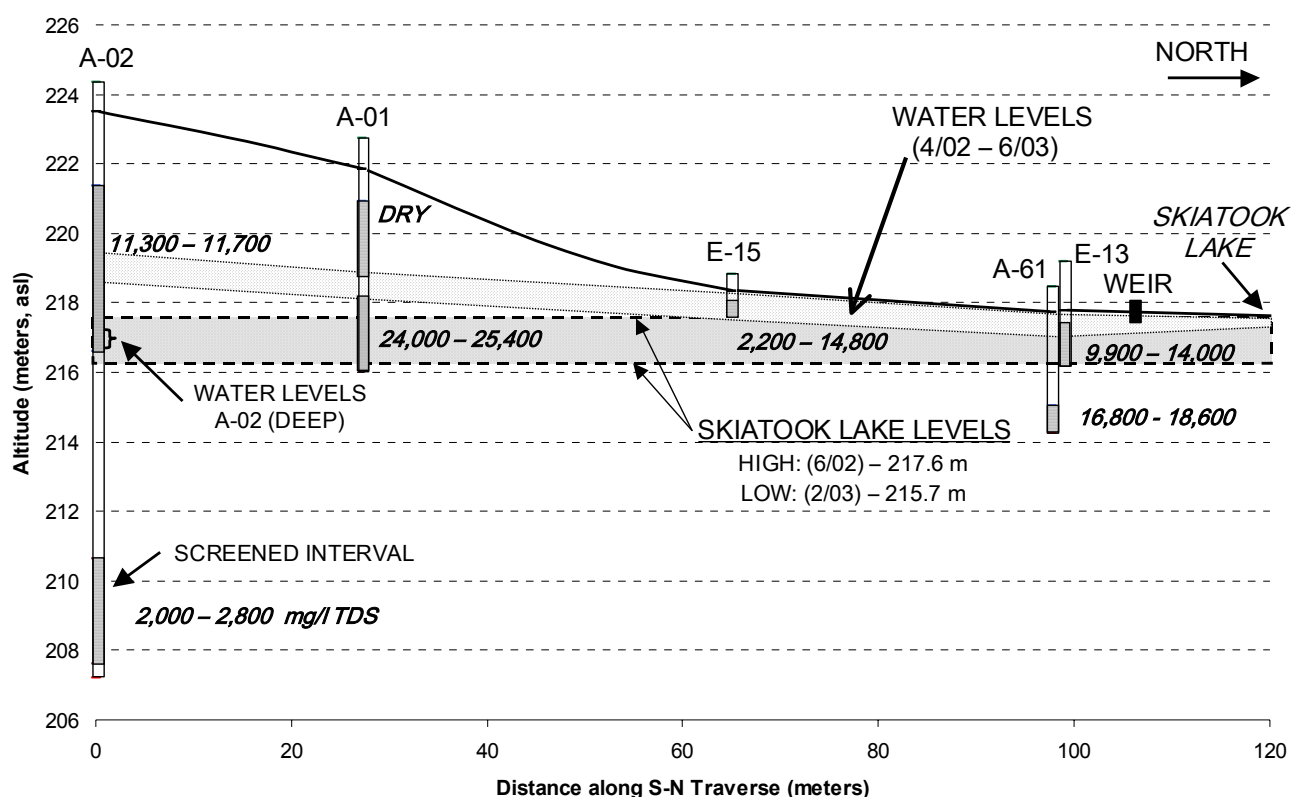


Figure 1. Salinity of contaminated groundwater in a S-N section of wells at the “A” site. The highest salinity is present at intermediate depths in well A-01, and extends to Skiatook Lake. The bottom of the plume is not currently defined, because water from the deepest screened interval (well A-02) has high organics and moderate salinity.

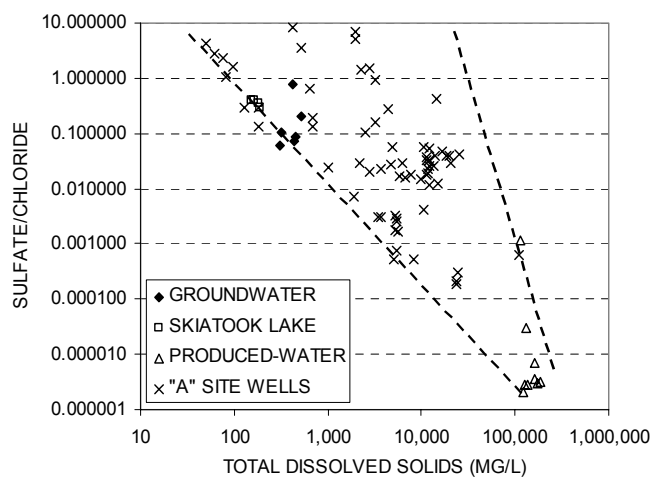


Figure 2. Oxidation of pyrite leading to sulfate increases relative to chloride in mixtures of produced water and pristine groundwater.

Results of sampling and geochemical modeling to date, however, show that the chemical composition of the plume water is determined not only by the mixing of produced water with pristine groundwater and percolating water from precipitation, but also by evapotranspiration, volatilization, sorption, mineral precipitation/dissolution, and bacterially mediated oxidation/reduction reactions. For example, the concentrations of sulfate relative to chloride increase (Fig. 2) because sulfate is mobilized by oxidation of pyrite that is abundant in shale beds. In deeper aquifers with high concentrations of dissolved organics, the conditions become reducing and sulfate is then reduced to sulfide. The sulfide produced, however, does not remain in groundwater, because it reacts with high concentrations of Fe^{++} to precipitate as iron sulfide.

Additional deep drilling is planned for January 2004 at the OSPER "A" site to map the depth and the horizontal boundaries of the 3-D plume of high salinity water shown in Figure 1. Monitoring of water levels, tracer tests and additional sampling of the existing and future wells will be carried out at this site. Ultimately we plan to use solute transport modeling to investigate the physical, chemical and biological processes controlling the transport of reactive and conservative solutes within the aquifers and from the aquifers into Skiatook Lake. Understanding the rates of the important natural processes at such sites is important to site restoration studies not only to petroleum sites in the Osage County, but throughout the USA and the World.

REFERENCES

- Carty, D.J., Crawley, W.W. & Priebe, W.E. 1997. Remediation of salt-affected soils at oil and gas production facilities: *American Petroleum Institute, Health and Environmental Services Department, API Publication Number 4663*.
- Energy Information Administration (EIA). 2003. *Annual Energy Outlook 2003, With Projections to 2025: Overview*. Washington DC.
- Godsy, E.M., Hostettler, F.D., Warren, E., Paganelli, V.V. & Kharaka, Y.K. 2003. The fate of petroleum and other organics associated with produced water from the Osage-Skiatook petroleum environmental research site, Osage County, Oklahoma. *US Geol. Surv. Water Res. Invest. Rep.* 03-4260: 85-103.
- Kampbell, D.H., An, Y.-J., Smith, M.W. & Abbott, M.A. 2003. Impact of oil production releases on some soil chemical properties at the OSPER field sites: *US Geol. Surv. Water Res. Invest. Rep.* 03-4260: 105-112.
- Kharaka, Y.K. & Hanor, J.S. 2003. Deep fluids in the continents: I. Sedimentary basins. In J. I. Drever (ed.), *Surface and Ground Water, Weathering & Soils, Treatise on Geochemistry* 5: 499-540.
- Kharaka, Y.K. & Otton, J.K. 2003. Introduction and summary. *US Geol. Surv. Water Res. Invest. Rep.* 03-4260: 1-13.
- Kharaka, Y.K., Thordsen, J.J., Kakouros, Evangelos, & Abbott, M.M. 2003. Fate of inorganic and organic chemicals in produced water from the Osage-Skiatook Petroleum Environmental Research sites, Osage County, Oklahoma. *US Geol. Surv. Water Res. Invest. Rep.* 03-4260: 57-84.
- Kharaka, Y.K., Thordsen, J.J. & Ambats, G. 1995. Environmental degradation associated with exploration for and production of energy sources in USA. In Y.K. Kharaka & O.V. Chudaev (eds.), *Water Rock Interaction (WRI-8)*: 25-30. Rotterdam, A. A. Balkema.
- Otton, J.K., Breit, G.N., Kharaka, Y.K. & Rice, C.A. 2002. A national produced-water geochemistry database: <http://energy.cr.usgs.gov/prov/prodwat/intro.htm>.
- Otton, J.K. & Zielinski, R.A. 2003. Produced water and hydrocarbon releases at the Osage-Skiatook petroleum environmental research studies, Osage county Oklahoma: Introduction and geologic setting. *US Geol. Surv. Water Res. Invest. Rep.* 03-4260: 15-42.
- Rice, C.A., Cathcart, J.D., Zielinski, R.A., & Otton, J.K. 2003. Characterization of soils and rock at an active oil production site: Effects of brine and hydrocarbon contamination. *US Geol. Surv. Water Res. Invest. Rep.* 03-4260: 137-150.
- Richter, B.C. & Kreitler, C.W. 1993. *Geochemical Techniques for Identifying Sources of Ground-water Salinization*. C. K. Smoley, CRC Press, Inc.
- Smith, B.D., Bisdorf, R.J., Horton, R.J., Otton, J.K. & Hutton, R.S. 2003. Preliminary geophysical characterization of two oil production sites, Osage county, Oklahoma-Osage Skiatook petroleum environmental research project. *US Geol. Surv. Water Res. Invest. Rep.* 03-4260, p. 43-56.
- USEPA (Environmental Protection Agency). 1987. Management of wastes from the exploration, development, and production of crude oil, natural gas, and geothermal energy. Volume 1 (oil and gas); volume 2 (geothermal). EPA/530-SW-88-003.